

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
29 January 2004 (29.01.2004)

PCT

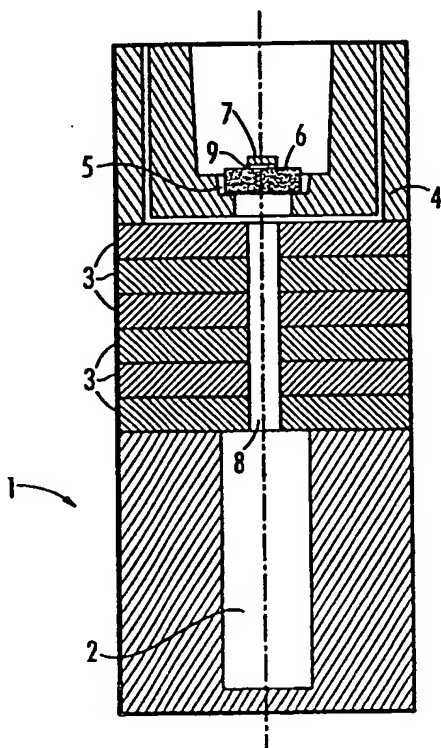
(10) International Publication Number  
WO 2004/009269 A2

- (51) International Patent Classification<sup>7</sup>: B22D 1/00, B22C 9/08, C21C 1/08
- (21) International Application Number: PCT/US2003/023151
- (22) International Filing Date: 24 July 2003 (24.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/398,268 24 July 2002 (24.07.2002) US
- (71) Applicants and  
(72) Inventors: CRAIG, Donald [US/US]; 134 Hawks Nest Drive, Fletcher, NC 28732 (US). BINGHAM, Karen [US/US]; 700 Shepherd Street, Hendersonville, NC 28792 (US). AUBREY, Leonard [US/US]; 58 Chestnut Ridge Road, Arden, NC 28704 (US).
- (74) Agents: HARDAWAY, John, B., III et al.; NEXSEN PRUET JACOBS & POLLARD, LLC, P.O. Box 10107, Greenville, SC 29603 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: IMPROVED PELLET ADHESIVE

(57) Abstract: A method for securing an inoculating pellet to a filter comprising the steps of: applying a molten hot melt adhesive (9) to a pellet (7). The filter (6) is contacted with the pellet. The molten hot melt adhesive is between the pellet and the filter.



WO 2004/009269 A2



**Declaration under Rule 4.17:**

— of inventorship (Rule 4.17(iv)) for US only

**Published:**

— without international search report and to be republished  
upon receipt of that report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**TITLE**  
**IMPROVED PELLET ADHESIVE**  
**BACKGROUND OF THE INVENTION**

Technical Field

5     **[0001]**       The present invention is related to an improved inoculation filter and inoculation filter system for inoculating cast iron late in the casting process and to improvements in the adhesion between the inoculant pellet and the filter.

Background

10    **[0002]**       Cast iron is an extremely versatile engineered material comprising iron-carbon-silicon alloys that have been used in many commercial applications including the manufacture of mechanical parts. The versatility of cast iron has led to the utilization of this material in many structural applications where the homogeneity and consistency of the iron will have a critical impact on the components performance. The casting of clean homogenous iron, specifically grey or ductile, is an essential step in the  
15    production of high quality engineered castings. Due to the importance of these cast items it is imperative that iron, specifically gray or ductile iron, be consistently cast with uniform morphology, with minimum included impurities and with properties that are reproducible.

20    **[0003]**       Cast iron has an unusual metallurgical structure. Most metals form a single metallic crystalline structure during solidification. Cast iron, however, has a far more complex morphology during solidification. The crystalline phases that form during solidification of cast iron are dependent on the rate of solidification. Most engineered castings desire the formation of crystalline graphite within the iron matrix during solidification. If the cast iron solidifies too rapidly primary iron carbides can  
25    crystallize within the casting. Primary iron carbide is a hard brittle phase that makes the iron very difficult to machine and changes the physical and mechanical properties of the primary cast iron. Primary iron carbides are commonly referred to as "chill". Carbon contained as iron carbides is generally considered to be detrimental in most iron castings whereas carbon present as graphite improves the physical and mechanical properties of  
30    cast iron. Carbon can crystallize as either iron carbide or graphite during solidification. The formation of either phase is driven by the rate of solidification and the degree of nucleation contained within the liquid iron. The rate of solidification is constrained by the geometry of the casting, the rate of heat extraction of the mold material and the amount of superheat of the iron contained when the metal entered the mold. The degree

of nucleation is constrained by the metallurgical history of the molten iron. Carbon present as graphite is an advantageous form and persuading carbon to crystallize as graphite is an ongoing goal of standard foundry operations. Graphite can be present in several morphological forms including spherical, as is the case with ductile iron, and  
5 flake-like, which is the case with gray iron.

[0004] Standard foundry metallurgical practice includes inoculation wherein the nucleation and growth of graphite is encouraged at the expense of iron carbide formation. Preferential nucleation greatly enhances the mechanical and physical properties of the finished casting. Inoculation is typically done by addition of an  
10 inoculating agent to either the pouring ladle, the metal stream or within the mold. The inoculating agent is typically added to the pouring ladle by pouring the granulated inoculating agent into the ladle when the ladle is filled with liquid iron, whereas the inoculant is added to the metal stream by injecting or spraying a finely divided powder of the inoculating agent in the molten metal stream as the molten metal enters the mold.  
15 It is typically desirable to add the inoculating agent to the molten metal as late as possible to minimize fading. Insufficient or improper inoculation is constantly at the forefront of losses due to poor quality in a foundry operation.

[0005] It may be preferred for the formed graphite to be spheroidal, if a spheroidal graphite cast iron called "SG" or "ductile" iron is required. Alternatively, a  
20 lamellar graphite cast iron is required for "LG" or "grey" iron. The essential prior condition to be met is to prevent the formation of primary iron carbide.

[0006] To this end the liquid cast iron is subject before casting to an inoculation treatment, which will, as it cools, favour the appearance of graphite rather than that of primary iron carbide.

25 [0007] The inoculation treatment is therefore very important. It is in fact well known that the effectiveness of inoculation, whatever the inoculants used, reduces with time and, generally, has already reduced by 50% after a few minutes. To obtain maximum effectiveness, one skilled in the art generally practices progressive inoculation, applying to this end several additions of inoculants at different stages of the  
30 development of the cast iron. The final addition is made in the mold as the molds are fed or even in the feed conduits of the molds by placing in the path of the liquid cast iron inserts constituted by an inoculant material. These inserts are generally used associated with a filter; in this case they generally have a perfectly defined shape in order to be able to be fixed in the filter, most often in an adapted cavity. These inserts of

defined shape are known as "pellets" or "slugs". We will denote by the name "filter inoculant package" the unit constituted by the pellet and the filter.

[0008] There are two types of pellets. "Molded" pellets are obtained by molding the molten inoculant. "Agglomerated" pellets are obtained from a pressed  
5 powder with generally very little binding agent, or even without binding agent.

[0009] Commercial inoculants create nucleation sites by seeding the liquid iron with highly reactive elements. The reactive elements combine with oxygen and sulfur dissolved within the liquid iron and the resultant reaction products precipitate out of solution to form nucleation sites for graphite during solidification. These nucleation  
10 products continue to grow within the melt until the metal has completely solidified. These particulates must be within a narrow size range in order to nucleate graphite crystal growth. Thus seeding the metal with the reactive elements as close to solidification as possible increases the probability that the precipitated particles remain within the narrow size window necessary for nucleation of graphite crystals. Formation  
15 of crystalline graphite is contrary to the kinetically favored products. The critical parameters which affect inoculation are not understood and are still the subject of academic debate. The ability of a skilled artisan to predict, and therefore improve, inoculation efficiency is very much desired in the art.

[00010] Pellet inoculation, wherein the molten metal is exposed to a pellet  
20 just prior to a filter, is known wherein a base material comprising minor amounts of calcium, aluminum, and rare earths are used. As the casting proceeds the inoculation efficiency changes with time due to the kinetics associated with dissolution of the inoculating agent from the pellet. Further complicating the problems of inoculation is the realization that various pour volumes and times are desired for manufacturing  
25 different parts with different sizes. If long pour times are utilized, the method of ladle inoculation is undesirable due to fading of the inoculant in the ladle. If short pour times are utilized, the time may be insufficient to allow for the onset of inoculation by pellet inoculation. The properties which allow for effective inoculation in the metal stream are not well understood and typically a suitable working range is developed by  
30 experimentation at great cost and loss of material.

[00011] The Daussan patent FR 2,692,654 describes a filter inoculant package wherein the pellet is obtained by agglomeration of powder at 0.5 to 2 mm preferentially. The efficiency of this filter inoculant package is quite limited.

[00012] The Foseco Patent EP 0 234 825 describes a filter inoculant package wherein the inoculant is presented in the form of a powdery non-agglomerated powder enclosed in a plastic pouch. This unit is more complex to manufacture and employs non-agglomerated powder whose wettability with respect to the liquid cast iron is not always well controlled.

[00013] Efforts to alleviate the problem of effective inoculation are presented in the art with limited success. DE Patent Publication DE 43 18 309 A1, for example, incorporates an inoculating pellet into a depression of a filter. The filter, in a honeycomb, comprises pores of 1 to 8 mm. The effectiveness of this type of filter inoculant package proves in use to be restricted by that of the pellet employed. This accomplishes the goal of inoculating late in the process but does not mitigate the primary issue associated with the process dependent inoculation efficiency described above. The pellet/filter combination has been found to be of limited value to foundries since it does not provide any benefit, other than localizing the pellet.

[00014] U.S. Pat. No. 6,293,988 provides an inoculating agent which comprises oxysulphides. The advantage provided is the elimination of ferrosilicon as a carrier medium. The oxysulphide inoculating agent dissolves slowly and the rate of inoculation, particularly early in the pour, may be inconsistent and unpredictable. A slowly dissolving pellet is subject to problems associated with inefficient inoculation early in the pour even though the problem of fade may be mitigated to some extent.

[00015] Inoculants utilizing ferrosilicon carriers are known to dissolve very rapidly and therefore their use for ladle inoculation is widely accepted. The rapid dissolution rate has caused ferrosilicon carrier based inoculants to be overlooked in the art due to the understanding that the rapid rate of dissolution would cause the pellet to be dissolved prior to the end of the pour and therefore the inoculant would not be effective throughout the entirety of the pour. The rapid dissolution rate has made the ferrosilicon based inoculant difficult to control.

[00016] Prior to the present invention, artisans have been restricted to the use of ferrosilicon based inoculants in the ladle, injecting a stream of inoculant into flowing metal and non-ferrosilicon based inoculants as a pellet. Furthermore, the artisan has had to choose between fade, with ladle inoculation, ineffective inoculation early in a pour with pellet inoculation or the mechanical complexities associated with injection inoculation.

[00017] In commonly assigned co-pending U.S. Pat. Appl. No. 10/043,644 filed 1/10/2002, which is incorporated herein by reference thereto, an improved filter inoculation system was described which greatly enhances the ability to inoculate molten iron. The filter inoculation system utilizes a friction fit inoculant in a partially bored filter element. While this product greatly improves the art of inoculation several problems exist which have been mitigated in the present invention. The incorporation of a partial bore increases the manufacturing complexity thereby increasing cost. Furthermore, the additional manipulation increases spoilage. It would therefore be desirable to create a inoculant filter wherein the inoculant pellet is secured to the surface of the filter thereby obviating the need for a bore.

[00018] Yet another deficiency is the reliance on a friction fit pellet in the partial bore. The tolerances required to insure an adequate friction fit are difficult to reproduce consistently. Inconsistency results in spoilage and in material which must be reworked. The pellet also has a tendency to crumble, and/or become dislodged, during the insertion process. The problems of crumbling and dislodging are exasperated during shipping. The previously described material is difficult to transport with a friction fit inoculant and the losses due to the pellet becoming dislodged or damaged are unacceptable. There is a need for a method for securing the inoculant pellet to the filter without hindering the dissolution of the pellet.

[00019] There is a desire in the art for a filter comprising an inoculating agent, in the form of a pellet, which is stable and which is transportable and effective.

#### SUMMARY

[00020] It is an object of the present invention to provide an inoculating pellet for consistently inoculating molten iron over a wide working range of pour times without fade or ineffective inoculation and which can be easily transported.

[00021] It is an object of the present invention to provide an inoculation method wherein an inoculating filter element can be utilized in a stream of molten metal.

[00022] A particular feature of the present invention is reduction in the losses which occur during manufacturing and shipping.

[00023] Yet another particular feature of the present invention is the ability to minimize the necessity for a bore in the filter.

[00024] These and other advantages, as will be realized, are provided in a method for securing an inoculating pellet to a filter comprising the steps of: applying a

molten hot melt adhesive to the pellet; and contacting the filter with the pellet wherein the molten hot melt adhesive is between the pellet and the filter.

[00025] Yet another advantage is provided in a method for forming an inoculating filter. The method comprises the steps of forming a pellet by compressing a powdered inoculant into a cylinder. A ceramic filter is formed and a molten hot melt adhesive is placed between the filter pellet.

[00026] Yet another advantage is provided in an inoculating filter comprising: an inoculating pellet, a ceramic filter and a hot melt adhesive there between.

[00027] A particularly preferred embodiment is provided in a method for inoculating molten iron. The method comprises passing the molten iron through a filter assembly. The filter assembly comprises a filter element, an inoculation pellet and a hot melt adhesive between the filter element and the pellet.

#### BRIEF DESCRIPTION OF DRAWINGS

- [00028] Fig. 1 is a cross-sectional view of a test mold.
- 15 [00029] Fig. 2 is a top view of an inoculant pellet attached to a filter in the bore.
- [00030] Fig. 3 is a perspective view of an inoculant pellet attached on top of the filter.

#### DETAILED DESCRIPTION

20 [00031] The present invention relates to an inoculation system comprising an inoculation pellet in functional contact with a filter element and to a method for use which greatly increases the consistency with which molten metal, particularly iron, can be inoculated. The art of inoculation with a pellet has previously met with limited success. Non-ferrosilicon based pellets, such as those described in U.S. Pat. No. 25 6,293,988 dissolve slowly and the resulting cast iron still comprises chill levels which are consistent with inappropriate inoculation. The art lacks a teaching which provides a ferrosilicon based inoculant pellet which can be utilized over a broad range of flow rates, or approach velocities, with adequate inoculation and minimal fading and which can be manufactured and transported with minimal loss. Through diligent research such

30 teaching is provided herein.

[00032] The invention will be described with reference to the figures. Fig. 1 illustrates a test mold for preparing cast of molten iron for determination of effectiveness. The test mold, generally represented at 1, comprises a mold cavity, 2, into which the molten metal will flow and cool. Spacers, 3, are placed between the



mold cavity, 2, and an upper pouring cup 4. The filter, 6, and pellet, 7, are held into a funnel, 5. Molten metal is poured into the funnel, 5, whereby it passes through the filter and dissolves the pellet. The dissolution of the pellet imparts inoculants into the molten metal. The molten metal flow through the channel, 8, in the spacers, 3, and into the mold cavity, 2.

[00033] A pellet and filter are illustrated in top view in Fig. 2 and perspective view in Fig. 3. The pellet, 7, is secured to the filter by the adhesive, 9.

[00034] One skilled in the art who practices inoculation at the different stages of the development of the cast iron uses products which are all the finer the later the inoculant is added in the process. The logic is that upstream the products have all the time necessary to dissolve and that when they reach the inlet of the molds they have only a few seconds left before solidification.

[00035] Granulated 2 to 10 mm particles are currently used in pre-inoculation, 0.2 to 2 mm granulated particles are used during ladle treatment, and 0.2 to 0.7 mm granulated particles are used for stream inoculation when casting. The applicant has in fact noted an unexpected phenomenon in the testing shop. For a same dosing of inoculant, the number of graphite nuclei generated in the liquid cast iron increases with the number of inoculant particles added to the inoculant mass unit. Therefore, if two ladles of cast iron are treated in identical conditions with a same inoculant in two different particle size distributions, the cast iron treated with the finest product will contain more graphite nuclei than that treated with the coarser product. These nuclei will also be smaller in size.

[00036] The same phenomenon has been observed during an in the mold treatment with agglomerated pellets. The cast iron treated with a pellet obtained from a finer powder will contain more graphite nuclei than that treated with a pellet obtained from a coarser powder. These nuclei will also be smaller in size.

[00037] To obtain pellets in this way which have maximum effectiveness in terms of inoculation, the applicant has been led to prepare powders at 0 to 2 mm having a particular internal particle size distribution defined in the following way: passing to 2 mm:100%; passing between 50  $\mu$  and 250  $\mu$ : 30 to 70%, more preferably 40 to 60%; fraction below 50  $\mu$ : less than 25%, more preferably less than 20%.

[00038] A powder of this type agglomerates easily which makes it possible to operate with lower proportions of binding agent. Thus with sodium silicate, which is a well known binding agent, doses of 0.3 cm<sup>3</sup> for 100 g of powder to 3 cm<sup>3</sup> for 100 g of

powder are sufficient according to the pressures employed which may vary from 50 to 500 MPa since the mechanical performance of the pellets is easily acquired. The pressure and binding agent percentage parameters may be used to control the dissolution speed of the pellet and not its mechanical performance.

5     [00039]       Experience shows that the particle size distribution defined above cannot be obtained by natural crushing. The preparation of powder of this particle size distribution requires a dosing of size fractions prepared in isolation.

10    [00040]       The filter associated with the pellet is a ceramic filter comprising continuous or semi-continuous voids or passageways which the metal passes and in which any included particles larger than  $10\ \mu$  and preferably  $3\ \mu$  become lodged.

15    [00041]       Controlling the dissolution rate to allow for a wide range of flow rates, or approach velocities, now allows for predictable inoculation without regard for approach velocities within a working range of 1-60 cm/sec measured at  $30.25\ \text{cm}^2$  flow cross-section.

20    [00042]       The effective component of the present invention comprises a ferrosilicon carrier and at least one active element. The ferrosilicon carrier is a low-active element which dissolves in molten iron without significantly forming seed nuclei. The active element is an element, or combination of elements, which dissolve in molten iron and react with elements in the molten iron to form seed nuclei upon which graphite preferentially crystallizes.

25    [00043]       The effective component of the inoculant pellet preferably comprises 40-99.9%, by weight, carrier and 0.1-60%, by weight active element. Particularly preferred carriers are prepared from ferrosilicon comprising non-reactive impurities. Ferrosilicon is available commercially from a variety of sources. Ferrosilicon is typically provided as 75% ferrosilicon which indicates, by nomenclature in the art, that the material comprises approximately 75%, by weight, silicon and 25%, by weight, iron. Ferrosilicon is widely available as 50% ferrosilicon which indicates that the material comprises approximately 50%, by weight, silicon and 50%, by weight, iron. For the purposes of the present invention the binder includes all non-inoculating elements. It is most preferred that the carrier comprise at least about 30%, by weight ferrosilicon. It is preferable to add a binder to the effective components prior to forming a pellet. The binder, such as sodium silicate, is well known in the art to assist in pellitization of a powder.

30

[00044] The active elements of the present invention include at least one rare earth or at least one inoculating agent chosen from the group consisting of cerium, strontium, zirconium, calcium, manganese, barium, bismuth, magnesium, titanium, aluminum, lanthanum and sulfur. Particularly preferred inoculating agents include at least one element chosen from the group consisting of strontium, aluminum, lanthanum, zirconium, calcium and manganese. The inoculant preferably comprises about 0.1-60%, by weight inoculating agent. More preferably, the inoculant comprises about 0.1-40%, by weight, active inoculating agent. Most preferably, the inoculant comprises about 0.1-20%, by weight, active inoculating agent.

[00045] Approach velocity is a practical measure, well known in the industry, to indicate the volume of metal flowing to, and through, a filter. As would be apparent to one of ordinary skill in the art the approach velocity is determined at a fixed cross-sectional flow area. For the purposes of the present invention all approach velocities are calculated at a cross-sectional area of  $30.25 \text{ cm}^2$  unless otherwise stated. It would be readily apparent to one of ordinary skill in the art that different cross-sectional areas would generate different approach velocities, however, the approach velocity could be easily compared to those cited herein by simple conversion as known in the art.

[00046] The dissolution rate of the inoculant is defined as the amount of inoculating agent consumed as a function of time. The analysis of certain inoculants is difficult therefore the dissolution rate is based on the analysis of a determinant element, either an inoculant or marker. The weight ratio of the determinant element to other inoculating agents is assumed to be the same in the cast iron as the weight ratio in the original pellet. For the purposes of the present invention zirconium is used as an inoculating determinate element. Therefore, the total inoculant in the cast iron is determined as the amount of zirconium plus other inoculants in the iron. For example, if an inoculant has 1 part zirconium, by weight, to 1 part manganese, by weight, and the amount of zirconium in the iron is 20 ppm then the amount of manganese will also be 20 ppm for a total inoculant of 40 ppm. The grams of zirconium plus manganese, which is present in an amount of 40 ppm, divided by the pour time is the inoculant dissolution rate.

[00047] An inoculant dissolution rate of at least approximately 1 mg/sec. is necessary to have sufficient inoculation for approach velocities of 1-60 cm/sec. Below 1 mg/sec. an insufficient inoculation rate is observed, particularly early in the pour, to insure minimum or no chill and to substantially eliminate the formation of iron carbide.

Alternatively, the approach velocity must be lowered to a level which is impractical with an inoculant dissolution rate below approximately 1 mg/sec. More preferably, the inoculant dissolution rate is no less than 10 mg/sec. More preferably, the inoculant dissolution rate is no less than 20 mg/sec. An inoculant dissolution rate of no more than approximately 320 mg/sec. is required to insure that the rate of dissolution is sufficiently slow to insure that pellet remains throughout the entire pour at approach velocities of 1-60 cm/sec. Above approximately 320 mg/sec. the pellet may dissolve prematurely thereby failing to inoculate the late portions of the pour. Alternatively, the approach velocity must be increased to a level which is impractical. More preferably, the inoculant dissolution rate is no more than approximately 250 mg/sec. Most preferably, the inoculant dissolution rate is no more than approximately 200 mg/sec.

[00048] Commercially available ferrosilicon based inoculants dissolve at a rate which exceeds 320 mg/sec. While imminently suitable for use in ladle inoculation these have been found to be unsuitable for use in a pellet at the point of filtration. Prior to the present invention the rate of dissolution for ferrosilicon based inoculants has not been explored due to the understanding in the art that the rate was too fast to be applied in this manner. The present invention illustrates that a ferrosilicon based inoculant can be prepared which, when prepared to a narrow range of dissolution rate, can be utilized as an inoculant pellet and the resulting cast iron has a low level of chill. Furthermore, the proper dissolution rate, which was previously not realized in the art, allows for superior inoculation with minimal inoculating agent. This substantially decreases the cost of inoculation and increases the predictability. Yet another advantage offered by the teachings herein is the ability to determine the proper amount of inoculant pellet to achieve a proper level of inoculation.

[00049] A dissolution rate of approximately 1 to approximately 320 mg/sec. allows for an inventive pellet to be used at approach velocities of 1-60 cm/sec. without fade or under inoculation in any portion of the pour. This is currently not available in the art without utilizing very large pellets which are only partially used or approach velocities which are undesirable. More preferably, the dissolution rate is approximately 1 to approximately 320 mg/sec. at approach velocities of approximately 1 to approximately 40 cm/sec. Even more preferably, approach velocities of 10 to 30 cm/sec. can be utilized and most preferably an approach velocity of 15-25 cm/sec. can be utilized with the preferred pellet dissolution rate of 2 to 250 mg/sec. A particularly preferred pellet dissolution rate is 2 to 150 mg/sec.

[00050] In a particularly preferred embodiment the dissolution rate of the pellet is determined at an approach velocity of 15 cm/sec. measured at a cross-sectional area of 30.25 cm<sup>2</sup>. At an approach velocity of 15 cm/sec. the pellet preferably has a dissolution rate of at least approximately 2 mg/sec. to no more than approximately 300 mg/sec. More preferably, measured at an approach velocity of 15 cm/sec. the pellet has a preferred dissolution rate of at least approximately 2 mg/sec. to no more than approximately 200 mg/sec.

[00051] The filtration rate of the filter can be adjusted between 0.01 kg/(s·cm<sup>2</sup>) and 0.5 kg/(s·cm<sup>2</sup>). More preferably between 0.04 kg/(s·cm<sup>2</sup>) and 0.24 kg/(s·cm<sup>2</sup>) according to the application.

[00052] Due to the inoculation rate generally required which is between 0.05% and 0.15% and due to the filtration capacity of the filter of the invention, which is between 1 and 1.5 kg of liquid iron per cm<sup>2</sup>, the filter inoculant package is sized with a ratio (pellet mass in g/filter surface in cm<sup>2</sup>) between 0.75 and 1.5. For instance, a filter inoculant package made of a 25 g pellet and a 30 cm<sup>2</sup> filter would be a convenient sizing.

[00053] The dissolution rate of the pellet is controlled by composition and packing density and particle size distribution. As the packing density increases the dissolution rate decreases. For the purposes of the present invention a ferrosilicon binder compressed to achieve a density of approximately 2.3 g/cc to approximately 2.6 g/cc is suitable to obtain the dissolution range required for the invention. Such a result can be obtained in adjusting the density of a pellet which can be obtained between 60% and 80% of the true density of the inoculant alloy the pellet is made of, depending on the pressure used for agglomerating which can vary from 50 to 500 MPa. Filter inoculant packages according to the invention, may be sized for the treatment of molten iron flow rates between 1 and 25 kg/s.

[00054] Ceramic filter elements are porous members comprising continuous or semi-continuous voids or passageways through which the metal passes and in which any included particles become lodged. The porous ceramic filter elements are preferably prepared by the manner described in U.S. Patent No. 4,056,586, which is incorporated herein by reference. Further elaboration on methods for manufacturing ceramic filter elements is provided in U.S. Patent Nos. 5,673,902 and 5,456,833, both of which are included herein by reference.

[00055] Typical hot melt adhesives are made with a base polymer which is a polymeric thermoplastic material which is solid at about 70°F. The base polymer is typically compounded with one or more tackifiers and preferably one or more waxes. The low-density hot melt adhesives are typically made by adding a low-density filler to a hot melt adhesive. The preferred base polymers are the following, or mixtures thereof: polyethylene, polypropylene, polybutene, ethylene-vinyl acetate (EVA), ethylene ethyl acrylate, ethylene-acrylic acid, ethylene propylene copolymer, ethylene propylene butene terpolymer and styrene block copolymer. Generally, EVA is preferred over polyethylene as a base polymer. Typically one or more tackifiers are added. They lower the viscosity and provide tack or adhesion. These tackifiers should be compatible with the base polymer, should not separate upon standing in liquid or molten form, and are preferably highly oxidatively stable. Among the naturally-occurring resins which may be used are polyterpenes, rosins, rosin esters and derivatives thereof. Hydrocarbon resins, particularly those with 5 and 9 carbons, terpenes, terpene/phenolics, polymerized a- and b- pinenes, rosin-modified phenolic resins, polymerized rosin, rosin derivatives, such as hydrogenated and dimerized rosins, and tall oil rosins may be used as tackifiers. Various synthetically-produced tackifying resins may also be employed, examples of which include aliphatic and aromatic hydrocarbon resins. Examples of other resins which may be used included modified terpenes, coumarone-indenes, polyesters, alkyl phenols, and styrene oligomers. Mixtures of tackifiers may also be used. The tackifier is present in an effective amount, to lower the melt viscosity of the composition and improve its ability to wet the substrate, thereby improving adhesion to the substrate. One percent tackifier, by weight, is particularly suitable. Hot melt adhesive compositions may contain at least 1 weight percent of one or more wax, which are generally low-melting hydrocarbon materials. Waxes may be included to raise or lower the softening point, to improve set times of the adhesive composition, to alter its viscosity, to improve handling characteristics and/or to increase the hardness of the bond provided. Suitable waxes include low molecular weight polyethylene, microcrystalline wax, Fischer-Tropsch wax, synthetic hydrocarbon wax, paraffin wax, and mixtures of these waxes. Preferred hot melt adhesives include 10-99.7%, by weight, more preferably 20-80%, by weight, more preferably 30-60%, by weight base polymer; 0-85%, by weight, more preferably 10-50%, by weight, tackifier; 0-50%, by weight, more preferably 0-20%, by weight, more preferably 5-15%, by weight, wax and 0-10%, by weight, more preferably 0.5-5%, by weight, and more preferably 1-3%, by weight low

density filler. The weight percent of low-density filler may vary beyond these ranges depending on the density thereof. Hot melt adhesives, tackifiers and waxes are well known in the art as exemplified in U.S. Pat. Nos. 5,672,677; 5,454,909; 5,026,752; 4,882,414; 4,853,460 and 4,283,317 all of which are incorporated by reference.

5 EXPERIMENTAL

[00056] Examples 1 to 5 are related to ductile cast irons. Example 6 is related to grey cast iron

EXAMPLE 1

[00057] A batch "A" of commercially available agglomerated inoculant pellets of the prior art was acquired and analyzed. The analysis gave: Si=72.1%, Al=2.57% and Ca=0.52%. A batch of molten inoculant of analysis as close as possible to that of the previous batch was synthesized in the induction furnace from FeSi 75, the strength of which was corrected by adding calcium silicide, aluminum then iron. This batch of inoculant was then cast in 25 g molded pellets. Sampling and analysis of this batch of pellets designated "B" gave: Si=72.4%, Al=2.83% and Ca=0.42%. A series of 30.25 cm<sup>2</sup> square silicon carbide ceramic filters were prepared using standard techniques. An organic foam was coated with a ceramic slurry such that all voids were filled. The organic foam was then compressed to expel excess slurry. The coated organic foam slurry was then dried and fired. A circular void, 24 mm in diameter, was cut partially into a surface of the filter for fitting of the pellet.

EXAMPLE 2

[00058] A charge of cast iron was melted in the induction furnace and treated by the Tundish Cover process by means of an alloy of the FeSiMg type with 5% Mg, 2% Ca, and 2% total rare earths (TRE) at the dose of 20 kg for 1600 kg of cast iron. The analysis of this liquid cast iron gave: C=3.7%; Si=2.5%, Mn=0.09%, P=0.03%, S=0.003%, Mg=0.042%. Its eutectic temperature was 1141°C. This cast iron was used to cast parts with a unit mass of about 1 kg, placed in clusters in a 20 part mold fed by an inflow conduit in which was placed a molded pellet of batch "B". The number of graphite nodules observed by metallography on the cross-section of the parts was 184/mm<sup>2</sup>.

EXAMPLE 3

[00059] Example No. 2 was reproduced in an identical way with the sole difference that the molded slug coming from batch "B" was replaced with an agglomerated pellet according to the prior art obtained by pressing a powder 0 to 2 mm

obtained by natural crushing of molded pellets taken from the same batch "B" as the pellet used in the previous example. The particle size distribution of this powder was: passing to 2 mm: 100%; passing to 0.4 mm: 42%; passing to 0.2 mm: 20%; passing to 50  $\mu$ : 10%, i.e. a particle size distribution quite close to that recommended in EP 0 234

5 825. The number of graphite nodules observed by metallography on the cross-section of the parts was 168/mm<sup>2</sup>.

#### EXAMPLE 4

[00060] Example No. 3 was reproduced in an identical way with the sole difference that the molded slug came from batch "A". The number of graphite nodules  
10 observed by metallography on the cross-section of the pellets was 170/mm<sup>2</sup>.

#### EXAMPLE 5

[00061] Example No. 3 was repeated with the following conditions. A 25 kg batch of molded slugs from batch "B" was crushed to 0 to 1 mm. The fractions 0.63 to 1 mm; 0.40 to 0.63 mm; 0.25 to 0.40 mm; 0.050 to 0.25 mm and 0 to 0.050 mm were  
15 separated by screening. Obtained was 3.5 kg of 0.63 to 1 mm; 3.9 kg of 0.40 to 0.63 mm; 4.2 kg of 0.25 to 0.40 mm; 7.1 kg of 0.050 to 0.25 mm and 6.1 kg of 0 to 0.050 mm. A powder was prepared by blending: 2 kg of 0.63 to 1 mm; 2 kg of 0.40 to 0.63 mm; 2 kg of 0.25 to 0.40 mm; 7 kg of 0.050 to 0.25 mm; and 2 kg of 0 to 0.050 mm. To this 15 kg powder blend was added: 150 cm<sup>3</sup> of sodium silicate and 150 cm<sup>3</sup> of 10  
20 normal sodium hydroxide. The blend obtained was used to manufacture cylindrically shaped agglomerated pellets 24 mm in diameter, 22 mm thick. The pressure exerted on the pellet to shape it was 285 MPa for 1 second. The shaped pellets were stored at 25°C for 8 hours in a carefully ventilated location and were then oven dried at 110°C for 4 hours. The pellets obtained, of 25 g unit mass, constituted a batch denoted batch "C".  
25 Example No. 3 was then repeated with pellets coming from batch "C" assembled with a ceramic foam filter identical to that used in example No. 2. The number of graphite nodules observed by metallography on the cross-section of the parts was 234/mm<sup>2</sup>.

#### EXAMPLE 6

[00062] Example No. 5 was repeated with the following conditions. A charge  
30 of 1600 kg of cast iron was melted in an induction furnace. A sample was taken of the liquid metal and analyzed. The analysis gave: C=3.15%, Si=1.82%, Mn=0.71%, P=0.15%, S=0.08%. The eutectic temperature was 1136°C. The cast iron was used to cast parts with a unit mass of about 1 kg, placed in clusters in a 20 part mold fed by an inflow conduit in which was placed a molded pellet supported by a 30.25 cm<sup>2</sup> filter



constituted by a refractory foam identical to the ones used in the other examples. The molded slug was from batch "C". The number of eutectic cells observed by metallography on the cross section of the part was 310/mm<sup>2</sup>.

#### EXAMPLE 7

5     [00063]     A series of 30.25 cm<sup>2</sup> square silicon carbide ceramic filters were prepared using standard techniques. An organic foam was coated with a ceramic slurry such that all voids were filled. The organic foam was then compressed to expel excess slurry there from while leaving the organic foam coated with slurry. The coated organic foam slurry was then dried and fired. A circular void, approximately 25.4 mm in  
10   diameter, was cut partially into a surface of the filter for fitting of the pellet.

      [00064]     A series of cylindrical pellets, approximately 20.5 mm in thickness and approximately 25.4 mm in diameter were prepared creating an alloy of active ingredients with silicon and iron. The alloy was melted, crushed, pulverized, sized and mixed with sodium silicate to form a pellet. The powder was placed in a mold and  
15   compressed to a level sufficient to obtain the density required of approximately 2.3 to 2.6 g/cc. The pellet was then inserted into the circular void of the ceramic filter.

      [00065]     A test mold comprising 5 chambers of equal size wherein each chamber is filled sequentially in a single pour was used to determine the dissolution rate of the pellet/filter combination throughout the pour. The pellet/filter combination was  
20   inserted into the test mold prior to the chambers and 29.51 Kg of molten iron was poured into the mold over different periods of time. Temperatures during the pour were determined to range from 1335-1470°C with no significant difference noted within this range of temperature.

      [00066]     Multiple core samples were taken from plates cast in the first, third  
25   and fifth chambers of the test mold and the core samples were dissolved and analyzed for zirconium by inductively coupled plasma spectrometry. The average zirconium level was defined as the Average Inoculation (AI). The Approach Velocity (AV), which is the velocity of metal at the leading edge of the filter was calculated from the following equation:

30     
$$AV = PW / (D * EFA * t)$$

where PW is the pour weight in grams; D is metal density in grams per cubic centimeter, EFA is effective filter area in cm<sup>2</sup>, or the surface area of the filter which is not covered by pellet and t is time in seconds. The average dissolution rate (ADR) was determined

as the total grams of inoculating agent consumed by the metal, based on the analysis of zirconium, over the total pour time. The results are provided in Table 1.

[00067] After the pour was complete the pellet was no longer visible on the filter. The presence of adequate inoculation in the first and last plates indicated that the  
5 dissolution rate was sufficient to effectively inoculate the entire pour without chill due to poor inoculation in any sample.

[00068] Analysis of the cast iron indicated that all of the inventive samples had adequate inoculation as indicated in the average inoculation (AI) which is based on the level of zirconium in the cast iron.

10 [00069] Table 1:

Sample	AV (cm/sec.)	AI (ppm Zr)	ADR (g/sec.)	Pour Time (sec.)
1	27.45	27	0.3104	7
2	21.35	17	0.149	9
3	19.21	15	0.1234	10
4	17.47	25	0.1854	11
5	17.47	17	0.1244	11
6	16.01	14	0.0939	12
7	14.78	14	0.0867	13
8	13.72	15	0.0862	14
9	13.72	20	0.1169	14
10	12.81	20	0.1091	15
11	12.81	12	0.0644	15
12	12.81	19	0.1022	15
13	12.81	15	0.0823	15
14	12.81	16	0.0876	15
15	12.01	26	0.1325	16
16	12.01	15	0.0771	16
17	12.01	14	0.0687	16

18	11.3	19	0.09	17
19	11.3	20	0.0963	17
20	10.67	15	0.0686	18
21	10.67	19	0.0864	18
22	9.61	16	0.0657	20
23	7.68	24	0.0762	25
24	7.68	23	0.074	25
25	7.39	19	0.0588	26
26	7.12	18	0.0537	27
27	7.12	18	0.0527	27
28	6.4	17	0.0447	30
29	4.8	21	0.0416	40
30	4.09	14	0.0234	47

## COMPARATIVE EXAMPLE

[00070] A ferrosilicon pellet was prepared as in the inventive example except the particle size and packing as commonly employed in ferrosilicon based inoculants.

- 5 The dissolution rate was estimated by pellet loss analysis and inoculant element percentage. The results are provided in Table 2.

Table 2:

Sample	AV(cm/sec)	ADR(g/sec.)	Pour Time(sec.)
C 1	14	0.349	6
C 2	17	0.42	5
C 3	16	0.42	5
C 4	13	0.349	6

The dissolution rate was too high to be an effective inoculant.

## COMPARATIVE EXAMPLE 2

[00071] A round inoculation disk with a diameter of 26.4 mm and a thickness of approximately 17 mm was inserted into a SELEE® silicon carbide filter. The inoculation disk comprised 15-49%, by weight, silicon; 7-22%, by weight, calcium; 2.5-10%, by weight, sulfur; 2.5-7.5%, by weight, magnesium and 0.5-5%, by weight, aluminum. Samples of 20kg-29kg Gray iron were poured through the filter at an approach velocity of approximately 12-18 cm/sec. After the pour was complete the remaining pellet was analyzed by SEM/EDS. A similar analysis was not possible with the inventive examples since the pellet was no longer distinguishable. The analysis suggested the formation of complex dross formations including silicates and sulfides of calcium magnesium aluminum compounds.

[00072] An independent analysis of cast iron utilizing the comparative pellet indicated formation of iron carbide with minimal formation of flake graphite thereby indicating ineffective inoculation.

[00073] It is apparent from the description and examples herein that effective inoculation can be accomplished utilizing ferrosilicon based pellets in contact with a filter element. It is unexpected that this combination would be suitable based on the knowledge in the art. Of further surprise is the observation that superior inoculation can be obtained wherein formation of carbides is substantially eliminated and chill control is excellent throughout the duration of a pour. This is an advance in the art which is contrary to the expectations of skilled artisans and based on manipulation of properties of ferrosilicon based inoculants which were previously not exploited based on the previously held belief in the art that pellet inoculation with ferrosilicon based pellets would expected to be undesirable.

## ADHESIVE EXAMPLES

[00074] To determine the effect that the binder system and the type of adhesives had on the dissolution of the inoculant tablet the following test procedure was followed. A series of test molds were produced and a different inoculant filter was placed in each test mold. An example of a test mold and test filter is shown in Fig. 1. Examples of the inoculant filter are shown in Figs. 2 and 3. The pellet is preferably cylindrical. Molten gray iron was poured into the pour basin above the inoculation filter and allowed to pass through the inoculant to pass through the inoculant filter assembly. The liquid iron was then captured in the reservoir, or mold cavity, at the base of the test

mold. Figure 1 shows a cross sectional drawing of the test mold used for this evaluation.

[00075] Once the test molds were poured they were allowed to cool to room temperature. The filter was then examined to determine if any residual inoculant was contained within the filter body. The dissolution of the inoculant tablet was ranked on a scale of 1 to 10. A rank of 1 represents no visible dissolution whereas a rank of 10 represents complete dissolution. The inoculant filter for this testing utilized a 15 g tablet comprising a binder and method of assembly as described in Table 3. The dissolution of the inoculant tablet was ranked for each tablet tested. Table 3 describes the set up and factors that were varied during the experimentation and the results. All experiments were repeated once to confirm test results. The results from the first heat and second heat were identical.

[00076] Table 3:

Test	Binder	Assembly Method	Diss. Rank	Observations
A	Sodium Silicate	Press fit, no adhesive, drilled filter body	10	Complete dissolution, no visible residue
B	Sodium Silicate	Press fit, no adhesive, drilled filter body	10	Complete dissolution, no visible residue
C	Sodium Silicate	Glued to top of filter with sodium silicate adhesive, no drilling in filter	7	Fair dissolution, some residual visible, pellet detached from filter
D	PVA	Glued to top of filter with sodium silicate adhesive, no drilling in filter	2	Minimal dissolution of edges, Not attached to filter
E	Gel Cast	Glued to top of filter with sodium silicate adhesive, no drilling in filter	4	Some dissolution at edges, pellet did not dissolve totally, not attached to filter
F	Sodium Silicate with a sodium silicate coating	Glued to top of filter with sodium silicate adhesive, no drilling in filter	1	No dissolution evident, not attached to filter

[00077] Table 4:

Test No.	Assembly Method
1	Hot Melt Adhesive A, adhesive placed at center of hole, Drilled filter body
2	Hot Melt Adhesive A, adhesive placed at 3 points on bottom of filter hole, drilled filter body
3	Hot Melt Adhesive A, adhesive placed on side of pellet in the hole, drilled filter body
4	Hot Melt Adhesive B, adhesive placed at center of hole, drilled filter body
5	Hot Melt Adhesive B, adhesive placed at 3 points on bottom of hole, drilled filter body
6	Hot Melt Adhesive B, adhesive placed on side of pellet in the hole, drilled filter body
7	PVA adhesive, adhesive placed at center of hole, drilled filter body
8	PVA adhesive, adhesive placed at 3 points on bottom of hole, drilled filter body
9	PVA adhesive, adhesive placed on side of pellet in the hole, drilled filter body

[00078] Table 5:

Test No.	Dissolution Rank	Observations
1	0	Adhesive failed during shipment
2	0	Adhesive failed during shipment
3	7	Some dissolution
4	0	Adhesive failed during shipment
5	0	Adhesive failed during shipment
6	9	Almost complete dissolution
7	0	Adhesive failed during shipment
8	0	Adhesive failed during shipment
9	1	No dissolution of tablet

[00079] Table 3 clearly shows that a change in the binder system decreases the dissolution rate of the inoculant tablet. This is undesirable. The tablets with PVA binder were more durable.

5 [00080] Table 3 also illustrates that the type of adhesive has an impact on the dissolution of the tablet. Sodium silicate is used as the binder and does not negatively impact the dissolution of the tablet. When sodium silicate was used as the adhesive it had a negative effect on the dissolution behavior of the tablet. Coating the tablet with sodium silicate completely retarded the dissolution behavior of the tablet. This is surprising due to the observation that the sodium silicate is a preferred binder. As  
10 indicated the adhesive, and the method of application, have a direct impact on the dissolution behavior of the inoculant tablet. This finding is unexpected.

[00081] Table 4 describes additional test factors. The test utilized a 15 gram pellet comprising a sodium silicate binder. All pellets were substantially identical. Three heatings were done to insure consistency in the data and observations. This  
15 dissolution of the inoculant tablet was ranked for each tablet tested. This ranking is listed in Table 5.

[00082] Heat 1 was done with a charge mix of gray iron returns (285 lb.) and steel punchings (7 lb.) for a total charge of 292 lbs. The chemical composition was determined to be CE, 3.89 %; C, 3.33%; and Si, 1.68%, by weight. The tapping  
20 temperature was 2652°F; the temperature in the ladle was 2604°F and the temperature at the end of the pour was 2502°F. The whole pouring cycle of 6 molds was approximately 3 min.

[00083] Heat 2 was done with a charge mix of gray iron returns (285 lbs.) and steel punching (10 lbs.) for a total charge mix of 295 lbs. The chemical composition  
25 was CE 4.04%; C, 3.39% and Si, 1.92%. The tapping temperature was 2654°F, the temperature in the ladle was 2613°F and the temperature at the end of the pouring was 2532°F. The whole pouring cycle of 6 molds was approximately 2 min 50 sec.

[00084] Heat 3 was done with a charge mix of 250 lbs. of gray iron returns. The chemical composition, by thermal analysis, was CE, 3.9%; C, 3.15%; and Si, 2.28%. The chemical composition, by spectrometer, was Mn, 0.45%; P, 0.025%; S,  
30 0.038%; Cr, 0.03%; Ni, 0.02% and Cu, 0.06%. The tapping temperature was 2850°F, the temperature in the ladle was 2556°F and the temperature at the end of the pouring was 2514°F. The whole pouring cycle of 3 molds was approximately 1.5 min.

[00085] Hot Melt Adhesive A is a hot melt EVA-based, medium setting, adhesive available as Hysol® Product 1942 from Loctite of Rock Hill, Ct. Hot Melt Adhesive A has a softening point of 198 °F (ASTM E28-67); a viscosity @350°F of 5000 cP (ASTM D 3236); a open time of 30 seconds; a heat resistance of 142 °F (ASTM D 4498), a specific gravity of 0.96 @ 77 °F (ASTM D 792); a tensile strength of 250 psi (ASTM D 638); an elongation of 500% (ASTM D 1876), a Tg of 7 °F (ASTM E 1640) and a "T" peel aluminum of 44 pli (ASTM D 1876).

[00086] Hot Melt Adhesive B is a hot melt EVA-based, medium setting, adhesive available as Hysol® Product 232 from Loctite of Rock Hill, Ct. Hot Melt Adhesive A has a softening point of 188 °F (ASTM E28-67); a viscosity @350°F of 11000 cP (ASTM D 3236); a open time of 15 seconds; a heat resistance of 153 °F (ASTM D 4498), a specific gravity of 0.96 @ 77 °F (ASTM D 792); a tensile strength of 150 psi (ASTM D 638); a Tg of -22 °F (ASTM E 1640) and an elongation of 1500% (ASTM D 638).

[00087] Table 5 illustrates that the type of adhesive and the method employed to apply the adhesive has an impact on both dissolution behavior of the tablet and the durability of the inoculant filter product. It is critical that the type of adhesive and the method used to apply the adhesive keeps the inoculant tablet firmly attached to the filter body. It was clearly evident that placing the adhesive at the bottom of the hole drilled in the filter body is ineffective in holding the tablet in place during shipment. Placing a bead of adhesive on the circumference of the pellet in a manner that allows good contact of the adhesive on both sidewalls of the filter and the tablet is an effective method of applying the adhesive. The finding that the method of applying the adhesive to the filter and or the inoculant filter was not expected to have such a dramatic effect on the transportation of the product.

[00088] Table 5 illustrates that the selection of adhesive does impact the dissolution behavior of the inoculant tablet. The PVA adhesive has a negative impact the dissolution of the tablet. The hot melt adhesives worked better than the PVA adhesive or the sodium silicate adhesive. Hot Melt Adhesive B is most preferred. The inoculant tablet dissolved almost completely in the test mold. This finding was completely unexpected and the fact that the type of adhesive would have such a dramatic effect on the dissolution behavior is not yet understood. The Hot Melt Adhesive B has been tested and found to work effectively in both the shipment of the inoculant filters and in the dissolution of the tablets in test castings.



Claimed is:

1. A method for securing an inoculating pellet to a filter comprising the steps of:  
applying a molten hot melt adhesive to said pellet; and  
contacting said filter with said pellet wherein said molten hot melt adhesive is  
5 between said pellet and said filter.
2. A method for forming an inoculating filter comprising the steps of:  
forming a pellet by compressing a powdered inoculant into a cylinder;  
forming a ceramic filter; and  
placing a molten hot melt adhesive between said filter and said pellet.
- 10 3. A method for inoculating molten iron comprising passing said molten iron  
through a filter assembly wherein said filter assembly comprises a filter element,  
an inoculation pellet and a hot melt adhesive between said filter element and said  
pellet.
4. The method of any of claims 1-3 wherein said pellet comprises a side and said  
15 molten hot melt adhesive is applied to said side.
5. The method of any of claims 1-4 wherein said pellet is cylindrical and said  
molten hot melt adhesive is applied to a face of said cylindrical pellet.
6. The method of any of claims 1-5 wherein said pellet has a mass, measured in  
grams, and said filter has a surface area, measured in  $\text{cm}^2$ , and a ratio of said  
20 grams to said surface area is at least 0.75 to no more than 1.5.
7. The method of any of claims 1-6 wherein said pellet comprises an active  
component comprising about 40-99.9%, by weight carrier comprising  
ferrosilicon and about 0.1-60%, by weight, and at least one inoculating agent  
selected from rare earths.
- 25 8. The method of claim 7 wherein said pellet comprises an active component  
comprising about 40-99.9%, by weight carrier comprising ferrosilicon and about  
0.1-60%, by weight, and at least one inoculating agent selected from a group  
consisting of cerium, strontium, zirconium, calcium, manganese, barium,  
bismuth, magnesium, titanium, aluminum, lanthanum and sulfur.
- 30 9. The method of claim 8 wherein said pellet has an inoculant dissolution rate of at  
least 1 mg/sec. to no more than 320 mg/sec.
10. The method of claim 9 wherein said pellet has an inoculant dissolution rate of at  
least 10 mg/sec.

11. The method of any of claims 1-10 where said hot melt adhesive comprises ethylene vinyl acetate.
12. The method of any of claims 1-11 wherein said hot melt adhesive comprises 10-99.7%, by weight, base polymer; 0-85%, by weight, tackifier; 0-50%, by weight, wax and 0-10%, by weight low density filler.
13. The method of claim 12 wherein said base polymer is ethylene vinyl acetate.
14. The method of any of claims 1-13 wherein said pellet is obtained by agglomeration of a powdered inoculant alloy and said filter is a refractory porous material, wherein said powdered inoculant of said pellet comprises a particle size distribution comprising 100%, by weight, less than 2 mm; 30-70%, by weight, between 50-250  $\mu$ , and less than 25%, by weight, below 50  $\mu$  and said filter only allows particles below 10  $\mu$  to pass there through.
15. The method of claim 14 wherein said filter only allows particles below 3  $\mu$  to pass there through.
16. The method of any of claims 1-15 wherein said pellet has an inoculant dissolution rate of at least 1 mg/sec. to no more than 320 mg/sec.
17. An inoculating filter comprising: an inoculating pellet, a ceramic filter and a hot melt adhesive there between.
18. The inoculating filter of claim 17 where said hot melt adhesive comprises ethylene vinyl acetate.
19. The inoculating filter of claim 17 wherein said hot melt adhesive comprises 10-99.7%, by weight, base polymer; 0-85%, by weight, tackifier; 0-50%, by weight, wax and 0-10%, by weight low density filler.
20. The inoculating filter of claim 19 wherein said base polymer is ethylene vinyl acetate.
21. The inoculating filter of any of claims 17-20 wherein said filter comprises a bore and said pellet is received in said bore.
22. The inoculating filter of claim 21 wherein said bore is a partial bore.
23. The inoculating filter of claim 22 wherein said partial bore is cylindrical comprising a base and a wall and said hot melt adhesive is between said pellet and said wall.
24. The inoculating filter of any of claims 17-23 wherein said pellet has a mass, measured in grams, and said filter has a surface area, measured in  $\text{cm}^2$ , and a ratio of said grams to said surface area is at least 0.75 to no more than 1.5.

25. The inoculating filter of any of claims 17-24 wherein said pellet has an inoculant alloy powder comprising between 40% and 60%, by weight, said between 50-250 $\mu$  and less than 20%, by weight, below said fraction below 50  $\mu$ .
- 5 26. The inoculating filter of any of claims 17-25 wherein said pellet comprises an active component comprising about 40-99.9%, by weight carrier comprising ferrosilicon and about 0.1-60%, by weight, and at least one inoculating agent selected from rare earths.
27. The inoculating filter of claim 26 wherein said pellet comprises about 0.1-40%, by weight, inoculating element.
- 10 28. The inoculating filter of any of claims 17-27 wherein said pellet has an inoculant dissolution rate of at least 2 mg/sec to no more than 250 mg/sec.

1/1

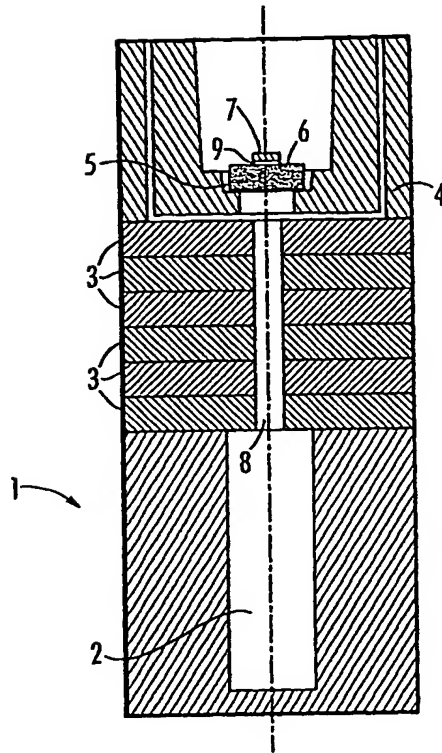


FIG. 1

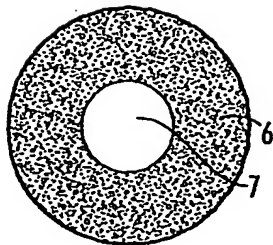


FIG. 2

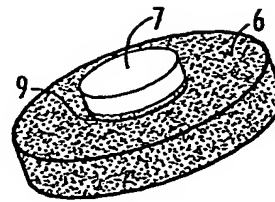


FIG. 3

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
29 January 2004 (29.01.2004)

PCT

(10) International Publication Number  
WO 2004/009269 A3

(51) International Patent Classification?: B22D 1/00,  
B22C 9/08, C21C 1/08

(21) International Application Number:  
PCT/US2003/023151

(22) International Filing Date: 24 July 2003 (24.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/398,268 24 July 2002 (24.07.2002) US

(71) Applicants and

(72) Inventors: CRAIG, Donald [US/US]; 134 Hawks Nest  
Drive, Fletcher, NC 28732 (US). BINGHAM, Karen  
[US/US]; 700 Shepherd Street, Hendersonville, NC 28792  
(US). AUBREY, Leonard [US/US]; 58 Chestnut Ridge  
Road, Arden, NC 28704 (US).

(74) Agents: HARDAWAY, John, B., III et al.; NEXSEN  
PRUET JACOBS & POLLARD, LLC, P.O. Box 10107,  
Greenville, SC 29603 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,  
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,  
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

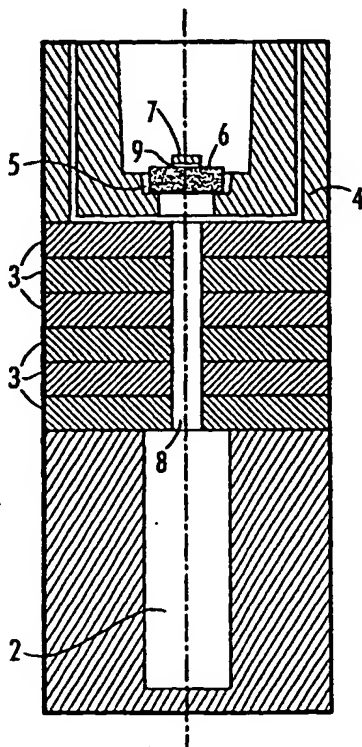
— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report

[Continued on next page]

(54) Title: METHOD FOR SECURING AN INOCULATING PELLET TO A FILTER AND INOCULATION FILTER THUS OBTAINED



(57) Abstract: The present invention is related to an improved inoculation filter and inoculation filter system for inoculating cast iron late in the casting process and to improvements in the adhesion between the inoculant pellet and the filter. Also disclosed is a method for securing an inoculating pellet to a filter comprising the steps of: applying a molten hot melt adhesive (9) to a pellet (7). The filter (6) is contacted with the pellet. The molten hot melt adhesive is between the pellet and the filter and comprises ethylene vinyl acetate.



(88) Date of publication of the international search report:  
24 June 2004

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 03/23151

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7    B22D1/00    B22C9/08    C21C1/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7    C21C    B22D    B22C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 18 309 A (SUEDEDEUTSCHE KALKSTICKSTOFF) 8 December 1994 (1994-12-08) cited in the application claims 1,6-8; figures	1-28
X	FR 2 691 654 A (DAUSSAN & CO) 3 December 1993 (1993-12-03) cited in the application claims; figures	1-28
A	EP 0 410 603 A (FOSECO INT) 30 January 1991 (1991-01-30) the whole document	1-3, 17-28
A	DE 16 08 051 A (STETTNER & CO) 22 October 1970 (1970-10-22) claims 1-3; figures	1-3,17
-/-		
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center;">24 March 2004</div>		Date of mailing of the international search report  <div style="text-align: center;">02/04/2004</div>
Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center;">Ceulemans, J</div>

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 03/23151

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 293 988 B1 (NARO RODNEY LOUIS) 25 September 2001 (2001-09-25) cited in the application the whole document -----	1-28



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 03/23151

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 4318309	A	08-12-1994	DE 4318309 A1	08-12-1994
FR 2691654	A	03-12-1993	LU 88124 A1	06-12-1993
			CA 2097261 A1	30-11-1993
			DE 69322006 D1	17-12-1998
			DE 69322006 T2	10-06-1999
			EP 0578517 A1	12-01-1994
			ES 2126637 T3	01-04-1999
			FR 2691654 A1	03-12-1993
			JP 6108170 A	19-04-1994
			KR 9607625 B1	07-06-1996
			US 5603373 A	18-02-1997
			US 5690161 A	25-11-1997
EP 0410603	A	30-01-1991	AU 629962 B2	15-10-1992
			AU 5981790 A	31-01-1991
			BR 9003621 A	27-08-1991
			CA 2021505 A1	27-01-1991
			EP 0410603 A1	30-01-1991
			JP 3066446 A	22-03-1991
			US 5033531 A	23-07-1991
			ZA 9005693 A	29-05-1991
			CA 2041437 A1	15-12-1991
DE 1608051	A	22-10-1970	DE 1608051 A1	22-10-1970
US 6293988	B1	25-09-2001	NONE	